would be to increase the fraction of nonattached cells by optimization of the homogenization or stomaching process. The second area is the exciting possibility of developing a separation protocol specific for single types of microorganisms, or a systematic or metabolic group of microorganisms. This may be achieved by manipulating the buoyant density of an organism through a selective uptake of a specific compound. Further, since it is possible to perform the separation on a micro scale, it may be feasible to design automated systems for sample preparation and analysis with a high sample capacity.

See also: **II/Centrifugation:** Theory of Centrifugation.

Further Reading

Anonymous (1992) *Percoll® Reference List*, 2nd edn. Sweden: Pharmacia P-L Biochemicals Inc.

Anonymous (1995) *Percoll® Methodology and Applications*, 2nd edn. Sweden: Pharmacia Biotech Inc.

Basel RM, Richter ER and Banwart GJ (1983) Monitoring microbial numbers in food by density centrifugation. *Applied and Environmental Microbiology* 45: 1156–1159.

Guerrero R, Mas J and Pedros-Alio C (1984) Buoyant density changes due to intracellular content of sulphur in *Chromatium warmingii* and *Chromatium vinosum*. *Archives in Microbiology* 137: 350–356.

Guerrero R, Pedros-Alio C, Schmidt TM and Mas J (1985) A survey of buoyant density of microorganisms in pure cultures and natural samples. *Microbiologia* 1: 53–65.

Kubitschek HE (1987) Buoyant density variation during the cell cycle in microorganisms. *Critical Reviews in Microbiology* 14: 73–97.

Lindqvist R (1997) Preparation of PCR samples from food by a rapid and simple centrifugation technique evaluated by detection of *Escherichia coli* O157:H7. *International Journal of Food Microbiology* 37: 73–82.

Lindqvist R, Norling B and Thisted Lambertz S (1997) A rapid sample preparation method for PCR detection of food pathogens based on buoyant density centrifugation. *Letters in Applied Microbiology* 24: 306–310.

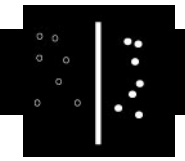
Payne MJ and Kroll RG (1991) Methods for the separation and concentration of bacteria from foods. *Trends in Food Science & Technology* 5: 384–389.

Pertoft H and Laurent TC (1968) The use of gradients of colloidal silica for the separation of cells and subcellular particles. In: Gerritsen T (ed.) *Modern Separation Methods of Macromolecules and Particles*, vol. 2, pp. 71–90. New York: Wiley Interscience.

Scherer P (1983) Separation of bacteria from a methanogenic wastewater population by utilizing a self-generating percoll gradient. *Journal of Applied Bacteriology* 55: 481–486.

DropBooks

FOOD TECHNOLOGY



Membrane Separations

M. Cheryan, University of Illinois, Urbana, Illinois, USA

Copyright © 2000 Academic Press

One of the earliest successful industrial applications of membrane technology was in the food industry. In 1972, a dairy plant in New York began processing cheese whey by reverse osmosis. Membrane separations are now ubiquitous in the food industry, as shown in **Table 1**. The main use of reverse osmosis is the concentration of liquid foods, to complement or replace evaporation. Nanofiltration is used for desalting and de-acidification with partial concentration, while ultrafiltration is used for fractionation, concentration and purification of food streams. Microfiltration is used for clarification and removal of suspended matter to replace centrifuges and filter presses. It is also used for pasteurizing and sterilizing liquids instead of using heat. Electrodialysis is finding use for demineralization and de-acidification, as a possible partial replacement for ion exchange. To date, pervaporation applications are few in the food industry, although it could be used for purification of volatile aroma compounds partially to replace distillation. This article focuses on selected food products with varying physical properties and chemical composition and will illustrate the general applicability of membrane technology in the food industry.

Dairy Industry

Milk

The dairy industry probably accounts for the largest share of installed membrane capacity among food-processing applications. **Figure 1** is a general schematic of possible applications of membranes in the processing of milk. Reverse osmosis (RO) is mostly used to preconcentrate milk prior to evaporation (although there are RO techniques that could concentrate skim milk up to 45% solids, as with the Freshnote process, described later). This not only saves sufficient energy to justify the technology, but it also

Table 1 Food industry applications of membrane technology

Dairy
RO: Preconcentration of milk and whey prior to evaporation; bulk transport; specialty fluid milk products
NF: Partial demineralization and concentration of whey
UF: Fractionation of milk for cheese manufacture; fractionation of whey for whey protein concentrates; specialty fluid milk products
MF: Clarification of cheese whey; defatting and reducing microbial load of milk
ED: Demineralization of milk and whey
Fruits and vegetables
Juices: apple (UF,RO), apricot, citrus (MF, UF, RO, ED), cranberry, grape (UF, RO), kiwi, peach (UF, RO), pear, pineapple (MF, UF, RO), tomato (RO)
Pigments: anthocyanins, betanins (UF, RO)
Wastewater: apple, pineapple, potato (UF, RO)
Animal products
Gelatin: concentration and de-ashing (UF)
Eggs: concentration and reduction of glucose (UF, RO)
Animal by-products: blood, wastewater treatment (UF)
Beverages
MF, UF: Wine, beer, vinegar – clarification
RO: Low-alcohol beer
Sugar refining
Beet and cane extracts, maple syrup, candy wastewaters – clarification (MF, UF), desalting (ED), preconcentration (RO)
Oilseeds, *cereals*, *legumes*
Soybean processing: Protein concentrates and isolates (UF); protein hydrolysates (CMR); oil degumming and refining (UF, NF); recovery of soy whey proteins (UF, RO); wastewater treatment (MF, UF, NF, RO)
Corn refining: Steepwater clarification and concentration (MF, UF, RO); light-middlings treatment: water recycle (RO); saccharification of liquefied starch (CMR); purification of dextrose streams (MF, UF); fermentation of glucose to ethanol (CMR); downstream processing of fermentation broths (MF, UF, NF, RO, ED, PV); wastewater treatment (MF, UF, NF, RO)

RO, reverse osmosis; NF, nanofiltration; UF, ultrafiltration; MF, microfiltration; ED, electrodialysis; CMR, continuous membrane reactor; PV, pervaporation.

exposes milk to less heat during the concentration process, which minimizes protein denaturation and development of the 'cooked' flavour and other heat-damaging effects on the constituents of milk.

Perhaps the greatest potential for RO and/or ultrafiltration (UF) in the dairy industry is in bulk milk transport, especially in those countries which have large distances between producing and consumption areas. Considering that milk is more than 85% water, preconcentration of the milk prior to shipment to central dairies should result in considerable savings in transportation costs, as well as reducing chilling and storage costs. RO milk products, when reconstituted with good-quality water, are indistinguishable from unconcentrated milks in flavour and other quality attributes. On-farm ultrafiltration of milk is technically feasible for large dairy herds if the concentrated milk is used for the manufacture of cheese. Stability of ultrafiltered milk is satisfactory with proper pretreatment such as thermalization at 65–70°C for 10–20 s to minimize lipase activity, and if health and safety requirements are met on the farm.

Ultrafiltration of milk RO milk could be used in the manufacture of several other products, such as cultured milk products and cheese. However, UF seems to be the preferred technique in these applications. UF allows the passage of the lactose and soluble salts while retaining the protein and fat and some of the insoluble or bound salts. There is considerable potential in the manufacture of specialty milk-based beverages such as lactose-reduced and calcium-enhanced fluid milk products. Total milk protein isolates are usually manufactured by co-precipitation using a combination of heat, acid and/or calcium salts. This generally results in low protein solubility, which restricts its use as a functional food ingredient. UF of milk in combination with diafiltration can produce 90% protein isolates from milk with lactose concentrations of less than 0.1%.

The principal use of milk UF in the dairy industry today is the manufacture of cheese. From a membrane technologist's point of view, cheese can be defined as a fractionation process whereby protein (casein) and fat are concentrated in the curd, while lactose, soluble proteins, minerals and other minor components are lost in the whey. In the UF cheese-making process, milk is first concentrated to a 'pre-cheese' which will have the same protein, fat and/or solid levels normally found in cheese. This pre-cheese is then converted to cheese by conventional or modified cheese-making methods. Some of the benefits of

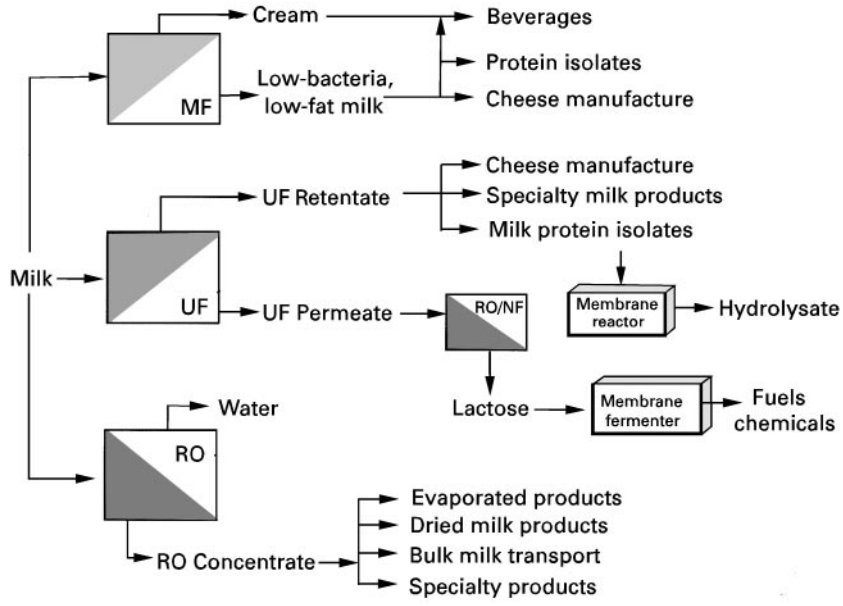


Figure 1 Membrane processing of milk. (Reprinted with permission from Cheryan and Alvarez (1995).)

using UF in cheese-making are:

- There is an increase in yield of 10–30% with soft and semi-soft cheeses due to the inclusion of the whey proteins
- The amount of enzyme (rennet) required is sometimes lower
- There is a reduced volume of milk to handle
- Fewer cheese-making vats are required
- Plant space is used better
- There is little or no whey production because most of the water and lactose has already been removed

Considerable research has been conducted with a variety of cheeses such as feta, quarg, white cheeses from Turkey, Egypt (domiati, kariesh), Greece (teleme) and South America (queso fresco), goat's milk cheese, Camembert, ricotta, mozzarella, cheddar and processed cheese.

Microfiltration of milk The main applications of microfiltration (MF) in milk processing are fat separation and bacterial removal. This concept has been put into commercial practice as the uniform transmembrane pressure (UTP) or co-current permeate flow (CPF) process. Tubular ceramic membranes with 1.4 μm pores are operated in a double-loop constant-pressure operation. Because of the uniform and low pressure profiles in the membrane module, fouling is low and flux is very high (700–1000 L m^{-2} h^{-1} at 10-fold concentration of skim milk). Bacterial retention is 99% and the microbial load usually found in milk and fat is also substantially rejected. On the other hand, there is no significant change in the concentration of other components, so the permeate is essentially bacteria-free skim milk.

This process became commercial in 1989 to produce more stable pasteurized and refrigerated milk products. It could also be useful in subtropical and tropical countries, where inadequate refrigeration and transportation facilities result in high microbial loads in the milk coming into dairy plants. Such a membrane system in the bulk-milk holding station or on the receiving dock of the milk-processing plant could lower the microbial load significantly and improve the quality of milk products in these countries.

Enriched casein fractions (i.e. separated from whey proteins and other soluble milk components without isoelectric precipitation) can be produced using MF membranes. In addition, β-casein can be isolated from casein micelles if the temperature is lowered to less than 5°C, which causes β-casein to dissociate from the micelle and be removed in the permeate (a loose UF membrane of 100 000 (molecular weight cut-off) can also be used to isolate β-casein from milk). This protein has biological activity potential in pharmotherapeutic applications.

Cheese Whey

Whey is a by-product of the cheese industry. During the manufacture of cheese, most of the milk protein (the casein) and fat is concentrated in the curd, which eventually becomes the cheese, while other constituents go into the water phase and become the whey. Every 100 kg of milk will give about 10–20 kg of

DropBooks

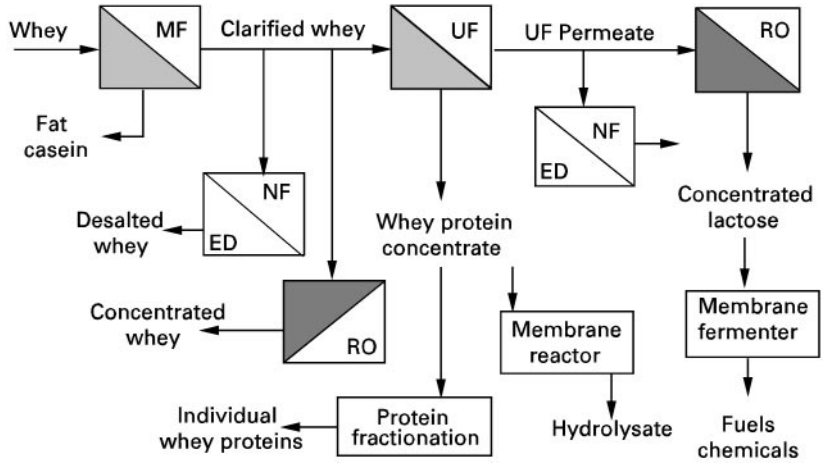


Figure 2 Membrane processing of cheese whey. (Reprinted with permission from Cheryan (1998).)

cheese depending on the variety, and about 80–90 kg of liquid whey. The disposal of whey is a problem: its biological oxygen demand (BOD) is 32 000–60 000 p.p.m. It has low solid content and a very unfavourable ratio of lactose to protein, which makes it difficult to utilize in food products without changing its composition. Prior to membrane technology, as much as 60–70% of the whey produced was disposed as sewage, with the rest being used primarily for animal feed or human food. World production in 1996 was estimated at 80–130 million tons per year: the USA produced about 30 million tons per year.

Membrane technology, and UF in particular, has provided a valuable means of upgrading cheese whey and increasing its utilization as a human food. The appropriate membrane can simultaneously fractionate, purify and concentrate whey components (**Figure 2**), enhancing their market value and reducing the pollution problem. Today, whey protein concentrates (WPC) produced by UF are well established in the food and dairy industries. Owing to the relatively mild process conditions of temperature and pH, the functionality of the whey proteins remains good, giving rise to a wide range of applications. The initial protein content of 10–12% (dry basis) can be increased by UF, to result in 35, 50 or 80% protein products, with a concomitant decrease in lactose and some salts. WPC can be further fractionated into β-lactoglobulin and α-lactalbumin fractions as shown, or be used for the manufacture of caseinomacropeptide, a compound which may have a pharmotherapeutic value.

Fruit Juices

Next to the dairy industry, fruit and vegetable juices have benefited the most from membrane technology. There are three primary areas where membranes can be applied in this application: firstly, clarification, e.g. in the production of sparkling clear beverages using microfiltration or ultrafiltration; secondly, concentration, e.g. using reverse osmosis to produce fruit juice concentrates of greater than 42° Brix (a measure of sugar concentration); and thirdly, de-acidification, e.g. electrodialysis or nanofiltration to reduce the acidity in citrus juices.

Clarification of Fruit Juice

Fruit juices are prepared by extraction followed by a series of filtration and clarification steps to yield clear single-strength juices (**Figure 3**). These operations are usually labour- and-time-consuming. Membrane filtration can replace the holding, filtration and decantation steps. The properties of the membrane, especially its pore size distribution, affect flux and capacity, as well as juice properties such as clarity, browning compounds and total phenolics in the finished product.

Membrane filtration has several advantages over traditional methods. It eliminates fining agents (bentonite, gelatin, etc.), most enzymes (pectinase, amylase), centrifugation and diatomaceous earth filtration. Process times are reduced from 12–36 to 2–4 h. Juice yields are higher, by 2–15%, and product quality is better. The largest application is apple juice, but the following have also received considerable attention: apricot, carrot, cherry, cranberry (which was one of the earliest applications of ceramic membranes), blackcurrant, grape, guava, kiwi, lemon, lime, maple sap, melon, orange, passion fruit, peach, pear, pineapple, plum, raspberry, strawberry and tomato.

Citrus juices (grapefruit, orange, lemon, lime) are being upgraded by combining UF and adsorbent resin

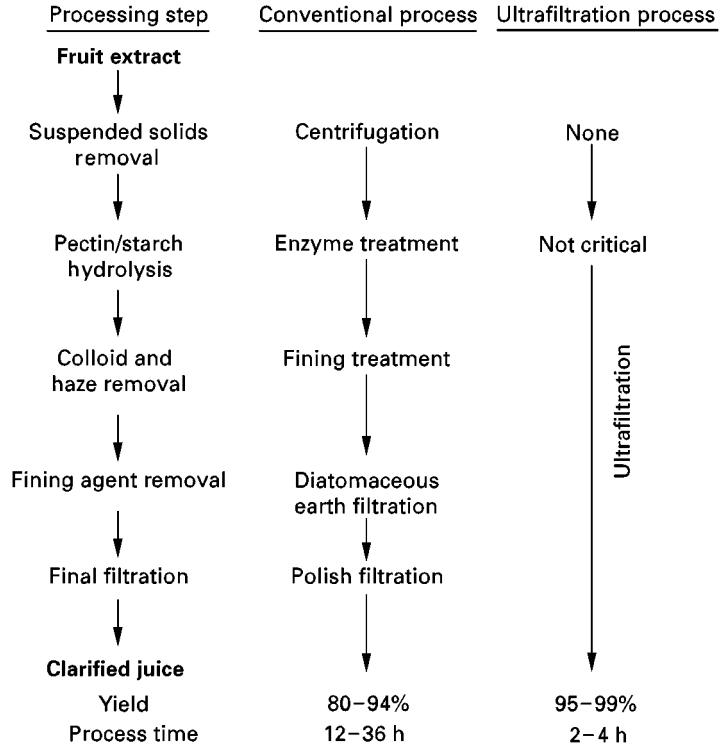


Figure 3 Processing fruit juices by conventional and membrane technology. (Reprinted with permission from Cheryan (1998).)

technology to remove bitter compounds such as limonin, naringin, hesperidin, polyphenols and many other off-flavour compounds. These compounds are in the aqueous phase of the juice. Fresh or reconstituted citrus juice which has been de-oiled and pasteurized is first ultrafiltered to separate the pulp. The clarified permeate containing the sugars and bitter compounds enters the absorption column which contains an adsorbent resin specifically designed to remove these compounds. The debittered juice is then recombined with the pulp (the UF retentate) to give a product with less than 5 p.p.m. limonin, which is its apparent taste threshold (400–500 p.p.m. for naringin).

In recent years, several fruit juice installations have incorporated ceramic membranes. The higher cost has been justified by the higher flux, much longer life and their resistance to aggressive processing and cleaning conditions. The ability to backflush to unblock feed channels and back-pulsing during operation are other advantages.

Concentration of Fruit Juice

Orange and other citrus juice concentrates are mostly produced by conventional multi-stage evaporation. RO with the appropriate polyamide composite membrane can concentrate juice without a significant loss of aroma, sugar or acids. The low temperatures avoid thermal damage of delicate aroma components. However, conventional RO is limited by osmotic pressure and viscosity considerations to less than 30° Brix. Therefore, RO can be used as a preconcentration step, with thermal evaporation completing the required concentration to 42–45° Brix. Adding RO ahead of the evaporators can increase evaporator capacity and reduce thermal treatment.

A significant development in the 1980s was the development of the FreshNote process by Du Pont and FMC. It allowed the production of highly concentrated (42–70° Brix) fruit juices using a combination of high and low retention RO membranes. UF is first used to separate the pulpy solids from the serum. The UF retentate, about 1/10th–1/20th the feed volume, is subjected to a pasteurization treatment that destroys spoilage microorganisms and improves stability of the finished product when blended back with the concentrated UF permeate. The serum (UF permeate), which amounts to about 90–95% of the feed volume, is concentrated by RO using hollow fine fibres made of aromatic polyamide. Pressures are typically 1000–2000 psi. A multistage system is used with high rejection membranes in the early stages and low rejection membranes in later stages. Permeates with significant sugar or flavour compounds are returned to stages containing high rejection membranes. Fruit juice concentrates of 45–55° Brix have been obtained commercially, and up to 70° Brix has been obtained in pilot trials. Careful control of

operating conditions is necessary. For example, the freshly extracted juice is blanketed with nitrogen and its temperature is controlled below 10°C throughout the remainder of the process. The flavour compounds in the serum are not subjected to any heat during processing, which also explains the high flavour scores for this product. Flavour and cost comparisons indicate very good market potential for this process. Commercial installations to date include tangerine juice and apple juice concentrates.

Concentration of tomato juice presents a difficult problem, because it has a high pulp content (25% fibre) and a high viscosity (which behaves in a non-Newtonian manner). Because of this, tubular modules are probably best. The colour of the final tomato concentrate is very good, and shows none of the browning normally associated with evaporation.

The interest in RO of maple syrup grew in the 1970s in response to increasing energy prices. RO is able to remove about 60% of water from the maple sap, resulting in a decrease of 33% in the processing cost compared to the all-thermal process. The concentrate is then boiled in a conventional open-pan evaporator to develop the characteristic colour and flavour.

Sugar Refining

The most appropriate application of membranes in this industry is for clarification and purification of the extraction juices. If UF or MF were used at the mill to remove the colloidal and macromolecular impurities, a clear decolorized thin juice would be obtained with little or no need for addition of lime, carbon dioxide or sulfite. If ion exchange is done immediately after UF, lime could be eliminated completely. An added benefit of membrane technology is that, with no macromolecules and reduced lime levels, fouling and scaling of the evaporator is reduced, which in turn reduces down time and cleaning costs. Higher yield of sugar and better crystallization are also possible: near-white sugar could be made in a single crystallization step. The MF or UF pretreatment is well suited for subsequent ion exchange softening and chromatographic purification. Another advantage is that a high quality soft cane molasses is obtained and this can go directly to chromatographic separation to recover sucrose and fructose, or to MF to remove some of the monovalent salts.

Another place in the sugar industry for UF or MF is to clarify thick juice (after evaporation), reducing bacterial counts and storage losses. Treating thick juice has the advantage of handling lower volumes, but this is partially compensated for by higher viscosity and lower flux.

Vegetable Proteins

Most of the work in this area has been done with soya beans. Once the oil has been removed from soya beans, the resulting meal is mostly used for animal feed, with perhaps only about 3–5% being used directly as human food. UF has been successfully used to upgrade the quality of the soy protein by selectively removing undesirable components such as oligosaccharides (implicated in gastrointestinal stress when consuming soya beans) and phytic acid (which forms insoluble chelates with minerals and can form complexes with proteins that reduce their bioavailability). To produce soy protein concentrates, the raw material is defatted soy flour which is extracted with dilute alkali. The extract is then ultrafiltered. The final composition will approximate to a soy protein concentrate of 70% protein, dry basis. To produce isolates (90% protein), the fibre and insoluble carbohydrate are removed by centrifugation or filtration prior to UF. The UF technique usually results in higher yields because of the inclusion of soy whey proteins that are normally lost in conventional manufacturing methods. These whey proteins could also be contributing to the superior functional properties of the UF soy products, in addition to the benefits of the nonthermal and nonchemical nature of the UF process.

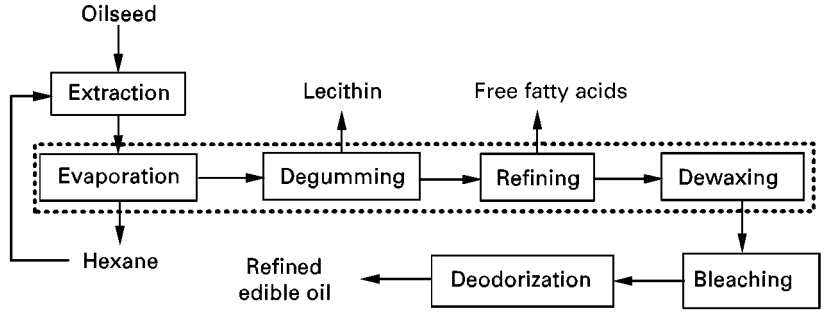


Figure 4 Edible oil processing. Membrane technology can be used in the four unit operations within the enclosed box.

Vegetable Oils

The basic unit operations in vegetable oil processing are shown in **Figure 4**. Oil is extracted from plant material (oilseeds) using a solvent, usually hexane. Published research indicates that about 50–70% of the hexane can be recovered and recycled using nanofiltration membranes instead of the evaporators used today, thus reducing energy consumption substantially. The extracted crude oil is mostly triglycerides, but it also contains small amounts of free fatty acids, phosphatides (lecithins/gums) and waxes, among other impurities. In place of physical or chemical refining, it is possible to use UF membranes for the degumming step, thereby producing a substantially oil-free lecithin.

In membrane refining, the crude oil is treated with a solvent such as methanol to extract the free fatty acids. After phase separation, the methanol layer is subjected to nanofiltration to recycle the methanol while producing a free fatty acid concentrate. This avoids the traditional alkali-refining process which results in soapstock formation and oil losses. Dewaxing with microfiltration membranes can also be done. In this process, the oil is cooled to a temperature below the wax crystallization temperature before being microfiltered to produce a stable edible oil. The application of membrane technology in the edible oil industry is expected to reduce energy consumption, reduce losses of oil, reduce the usage of chemicals and water and reduce the discharge of contaminated effluents.

Conclusions

The food industry is one of the largest users of membrane technology. With new developments in low-fouling membranes and modules, and membranes stable in organic solvents, the applicability of this technology will widen considerably in the industry, especially in the production of 'neutraceuticals' (minor compounds in plants that are thought to have considerable health benefits) and grain processing (e.g., corn, soyabeans, wheat).

Further Reading

Bhave RR (ed.) (1991) *Inorganic Membranes. Synthesis, Characteristics and Applications*. New York: Van Nostrand Reinhold.

Cheryan M (1992) Concentration of liquid foods by reverse osmosis. In: Lund DB and Heldman DR (eds) *Handbook of Food Engineering*, p. 393. New York: Marcel Dekker.

Cheryan M (1998) *Ultrafiltration and Microfiltration Handbook*. Lancaster, PA: Technomic.

Cheryan M and Alvarez J (1995) Membranes in food processing. In: Noble RD and Stern SA (eds) *Membrane Separations. Technology, Principles and Applications*, p. 415. Amsterdam: Elsevier.

Cheryan M and Nicholas DJ (1992) Modelling of membrane processes. In: Thorne S (ed.) *Mathematical Modelling of Food Processes*, p. 49. London: Elsevier.

Ho WSW and Sirkar KK (eds) (1992) *Membrane Handbook*. New York: Chapman and Hall.

Lloyd DR (ed.) (1985) *Materials Science of Synthetic Membranes*. Washington, DC: American Chemical Society.

Matsuura T (1994) *Synthetic Membranes and Membrane Separation Processes*. Boca Raton, FL: CRC Press.

Raman LP, Cheryan M and Rajagopalan N (1994) Consider nanofiltration for membrane separations. *Chemical Engineering Progress* 90: 68.

Renner E and El-Salam MH (1991) *Application of Ultrafiltration in the Dairy Industry*. New York: Elsevier.

Singh N and Cheryan M (1997) Membrane applications in corn wet milling. *Cereal Foods World* 42: 520.

DropBooks

Supercritical Fluid Chromatography

J. W. King, National Center for Agricultural Utilization Research, Agricultural Research Service/USDA, Peoria, IL, USA

The role of supercritical fluid chromatography (SFC) in the analysis of foods and agriculturally derived products has been somewhat moderated by uncertainties in the availability of required instrumentation for the past 15 years. In addition, SFC competes for the same analytical opportunities as gas (GC) and high performance liquid chromatography (HPLC) and hence is often ignored or relegated to a minor role by food analysts. Despite these difficulties, SFC has been applied to a variety of applications for the detection and quantification of analytes, that are at least soluble to even a minor extent in supercritical carbon dioxide (SC-CO_2) – by far the most popular mobile phase utilized in the technique.

The application of SFC to food matrices came naturally due in part to the early application of SC-CO_2 extraction in the food industry, i.e. for the